Pleurotus ostreatus spent mushroom compost as green biosorbent for nickel (II) biosorption

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ABSTRACT

The potential of Pleurotus ostreatus spent mushroom compost (PSMC) as a green biosorbent for nickel (II) biosorption was investigated in this study. A novel approach of using the half-saturation concentration of biosorbent to rapidly determine the uptake, kinetics and mechanism of biosorption was employed together with cost per unit uptake analysis to determine the potential of this biosorbent. Fifty per cent nickel (II) biosorption was obtained at a half-saturation constant of 0.7 g biosorbent concentration, initial pH in the range of 4–8, 10 min contact time, 50 mL 50 mg/L nickel (II) initial concentration. The experimental data were well fitted with the Langmuir isotherm model and the maximum nickel (II) biosorption was 3.04 mg/g. The results corresponded well to a second pseudo order kinetic model with the coefficient of determination value of 0.9999. Based on FTIR analysis, the general alkyl, hydroxyl or amino, aliphatic alcohol and carbonyl functional groups of biosorbent were involved in the biosorption process. Therefore, biosorption of nickel (II) must involve several mechanisms simultaneously such as physical adsorption, chemisorption and ion exchange. Cost comparison for PSMC with Amberlite IRC-86 ion exchange resin indicates that the biosorbent has the potential to be developed into a cost effective and environmentally friendly treatment system.

Key words | biosorbent, biosorption, half-saturation concentration, nickel (II), Pleurotus ostreatus spent mushroom compost

INTRODUCTION

Nickel is a frequently found waste compound in industrial wastewater especially from electroplating, mineral processing, non-ferrous metals and battery manufacturing. Though nickel has been shown to be essential for cellular growth and act as a co-enzyme of some living microorganisms or plants it can become mildly toxic and induces cellular oxidative stress if present in excessive amounts. Another important characteristic of nickel is it accumulates in the target organism, but does not become magnified along food chains. Hence, short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can represent a serious health hazard. In short, sources of nickel-containing wastewater require proper treatment to remove the threat that it poses to the environment (Chen et al. 2003; Cempel & Nikel 2006).

Conventional methods of heavy metal removal have certain disadvantages, such as high capital and operating costs or treatment and disposal of residual metal sludge (Volesky 2007). As a result, alternative treatment methodologies such as biosorption have been highlighted due to several factors that are seen as environmentally sustainable. Biosorption is a physical–chemical process that binds heavy metal ions by using non-living biological material. It is a green technology which utilizes biodegradable agricultural or industrial waste as biosorbent, plus the recovery of heavy metal ions from biosorbent is easily achieved by using diluted acid solution (Park et al. 2010).
In the agriculture sector, demand for mushrooms, especially oyster mushroom is ever growing (Singh et al. 2003; Tajbakhsh et al. 2008). Hence, *Pleurotus ostreatus* spent mushroom compost (PSMC), which is an agricultural waste generated by oyster mushroom cultivation, becomes an ever pressing issue. As a bulk solid waste, it requires further treatment prior to disposal. In practice, this material usually ends up being burnt in open fires in order to reduce the bulk of the waste so as to reduce the cost of solid waste disposal; a cost which is often seen as unnecessary by mushroom farmers. Therefore, the ability to utilize this waste as a biosorbent not only can help to lessen waste disposal issues of mushroom farms, but also promotes sustainability through the reuse of available resources. What makes this material ideal is the availability in bulk quantities, which is one of the main criteria for converting biomaterials for industrial use as outlined by Volesky (2007).

Despite the apparent potential of this waste, sadly there is a lack of information on the biosorption capability of PSMC in removing heavy metals from aqueous solution in the literature. Also, there are no attempts, to the authors’ best knowledge, in papers to establish a cost comparison ratio of a biosorbent with an ion exchanger of similar uptake capacity and uptake mechanism. Therefore, this paper presents three new ideas, i.e. (1) a rapid and simply approach in investigating the nickel (II) biosorption characteristics of PSMC from aqueous solution, utilizing the half-saturation concentration of biosorbent as a starting point to (2) study uptake, kinetic and mechanisms of the nickel (II) biosorption process of a novel biosorbent, together with (3) a simple cost comparison as a gauge of the potential practical use of this novel biosorbent in the water treatment industry.

**METHODOLOGY**

**Nickel (II) solution preparation**

Analytical grade of nickel (II) nitrate hexahydrate salt (Ni(NO₃)₂·6H₂O, Merck, Germany) was used to prepare nickel (II) solution with 18.2 MΩ cm ultrapure water.

**Biosorbent preparation**

The PSMC was collected from C & C Mushroom Cultivation Farm Sdn. Bhd., Johor, Malaysia. Sample was autoclaved for 15 min at 121°C, 18 psi and then dried in an oven at 60°C. It was ground and sieved to particle size <710 μm. The biosorbent was stored in a drying cabinet.

**Batch biosorption study**

All batch biosorption studies were conducted in duplicate. Briefly, the experiments were carried out with the biosorbent in Erlenmeyer flasks placed on an incubated shaker operating at 125 rpm, 50 mL nickel (II) solution and temperature of 25 ± 1°C. Parameters of 0.1–8.0 g biosorbent concentration, 1–8 initial pH, 0.5–30 min contact time and 10–250 mg/L initial nickel (II) concentration were examined. Samples were filtered and the supernatants were analyzed by ICP-OES (7300DV, Perkin Elmer, USA). Data for all samples analyzed were presented as mean ± 1SD.

**Comparison of PSMC with Amberlite IR-86 ion exchanger**

Amberlite IRC-86 (Dow Chemicals, USA) with similar mesh size to the PSMC (300–800 μm particle size) were prepared according to the manufacturer’s recommendation. Comparison of uptake capacity was done with optimized biosorption conditions obtained from the batch biosorption study, and all experiments were conducted in duplicate and data presented as mean ± 1SD.

**Statistical and mathematical analysis**

The percentage of nickel (II) biosorption was calculated by using Equation (1).

\[
\text{percentage of nickel (II) biosorption} = \left( \frac{C_o - C_f}{C_o} \right) \times 100\% 
\]

where \(C_o\), initial nickel (II) concentration (mg/L); \(C_f\), final concentration of nickel (II) concentration (mg/L).

The experimental data were fitted to the linear Langmuir plot of \(C_e/q_e\) versus \(C_e\) (Equation (2)).

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} 
\]

where \(q_e\), nickel (II) uptake by biosorbent (mg/g); \(q_{max}\), maximum nickel (II) uptake (mg/g); \(C_e\), nickel (II) concentration at the equilibrium stage (mg/L); \(b\), Langmuir constant (L/mg).
The nickel (II) biosorption was calculated from the pseudo-second order kinetics of Equation (3).

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

(3)

where \(q_e\), nickel (II) uptake by biosorbent at equilibrium (mg/g); \(q_t\), copper (II) uptake by biosorbent at time (mg/g); \(t\), time (minute); \(k_2\), rate constant of pseudo-second order (g/mg/min).

**Biosorbent characterization**

The specific functional groups in the biosorbent were identified with a Fourier Transform Infra-Red (FTIR) spectroscopy system (Series 100, Perkin Elmer, USA) using the ATR probe.

**RESULTS AND DISCUSSION**

Biosorption characteristics of PSMC were evaluated based on biosorbent concentration, initial pH, contact time, initial nickel (II) concentration as well as kinetic and isotherm analysis, physical characterization using FTIR, uptake and cost comparison with commercially available ion-exchange resin to ascertain the viability of the biosorbent as an alternative for nickel (II) contaminated water treatment. Since the standard deviation for all the experiments of this study did not exceed 2% of the average value, error bars were not shown on the figures, but values are provided within the respective tables.

**Biosorbent concentration**

Table 1 and Figure 1 show the effects of increasing biosorbent concentration on nickel (II) biosorption. The percentage biosorption of nickel (II) increased from 13 ± 0.28 to 89 ± 0.05% when biosorbent concentration was increased from 0.1 to 8.0 g. Initially, the increased biosorbent concentration which resulted in the increase of available active binding sites as well as the adsorptive surface area of biosorbent, bring about large increment in nickel (II) biosorption. However, further increase in biosorbent concentration did not effect a larger rise in biosorption. The initial rise in the biosorption percentage of nickel (II) could be attributed to the increase in binding sites available when the amount of biosorbent was increased. After the saturation stage, any further addition
of biomass would either increase the mass transfer resistance for the metal ions or bring about particle aggregation and coagulation of the biomaterial, which limits the accessibility of binding sites for biosorption. This phenomenon has also been observed by Shroff & Vaidya (2014) and Liu et al. (2013) for dead fungal biomass and pre-treated brown algae biosorbent respectively.

As the experimental data did not show a clearly defined saturation stage, half-saturation constant of nickel (II) biosorption was obtained by Michaelis–Menten derivation plot of Hanes–Woolf. The calculated half-saturation constant was found to be at 0.7 g biosorbent concentration as shown in Figure 2. This value was used in designing subsequent experiments in order to obtain reliable results rapidly and minimize the utilization of biosorbent. The use of biosorbents at the half-saturation constant concentration also allows for the study of other parameters such as pH, contact time and temperature without the interfering effect of limited binding sites.

Initial pH

The nickel (II) biosorption process is dependent on initial pH as depicted in Table 2 and Figure 3. The maximum nickel (II) biosorption of 47% was attained for initial pH ranging from 4 to 8. At low initial pH, active binding sites of biosorbent are being protonated and charge repulsion formed, thus resulting in reduced nickel (II) biosorption. When initial pH was increased, the active binding sites of biosorbent are deprotonated, thus strengthening the charge attraction leading to significant increase in biosorption. Findings recorded by Asadi et al. (2008) on modified ricehusk and sawdust biosorbent described a similar trend and order of magnitude for nickel (II) biosorption performance. In short, initial pH affects nickel (II) biosorption through the active binding sites of biosorbent and species of nickel (II). For further experimental design, initial pH was not adjusted since nickel (II) solution has the initial pH of 5.7 which represents the optimum range of nickel (II) biosorption.

Contact time

Table 3 and Figure 4 illustrate two phases of the nickel (II) biosorption process, starting with a rapid phase and then followed by an equilibrium phase. After 3 min of contact time, the equilibrium phase was achieved when 45% nickel (II) biosorption was observed. This reveals that active binding sites of biosorbent are easily occupied by nickel (II) ions
and achieved saturation stage at the equilibrium phase. A similar trend of observation involving biosorption studies using corn biomass and sawdust biomass was reported by Malkoc (2006) and Shukla et al. (2005). Based on these observations, subsequent experiments were conducted under equilibrium phase with 10 min contact time.

Initial nickel (II) concentration

The effect of initial nickel (II) concentration is shown in Table 4 and Figure 5. Biosorption of nickel (II) decreased from 68 ± 0.66% to 16 ± 0.03% as initial nickel (II) concentration increased from 10 to 250 mg/L. The increase in initial nickel (II) concentration had led to the increased number of nickel (II) ions competing for the biosorbent active binding sites. This resulted in reduction of nickel (II) biosorption. Besides that, initial nickel (II) concentration also functions as a driving force to overcome the mass transfer resistance for the biosorption process. This finding is consistent with studies reported by Malkoc & Nuhoglu (2005) where tea waste was used as a biosorbent.

<table>
<thead>
<tr>
<th>Initial Ni (II) conc. (mg/L)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (II) biosorption (%) ± 1SD</td>
<td>68 ± 0.66</td>
<td>62 ± 0.28</td>
<td>58 ± 0.07</td>
<td>52 ± 0.15</td>
<td>48 ± 0.68</td>
<td>44 ± 0.16</td>
<td>32 ± 0.86</td>
<td>25 ± 0.09</td>
<td>19 ± 0.38</td>
<td>16 ± 0.03</td>
</tr>
</tbody>
</table>

Langmuir isotherm

Regression analysis of the linearized model of the Langmuir isotherm is demonstrated in Figure 6 and was conducted to gain more insight into the biosorption of nickel (II) by...
PSMC. Based on the calculated slope and intercept, the maximum biosorption capacity, the Langmuir constant and coefficient of determination values were 3.04 mg/g, 0.058 L/mg and 0.9992 respectively. The Langmuir isotherm is well-founded for monolayer biosorption on the surface of biosorbent. By taking a high value of \( b \) in the Langmuir isotherm into consideration, the biosorbent shows a clear preference for binding nickel (II). This result is similar to those reported for biosorbent from esterified lemon, lignin and algae all of which corresponded well with the Langmuir isotherm (Romera et al. 2009; Arslanoglu et al. 2009). Specificity for a particular cation is desirable as it allows targeted removal of contaminating heavy metal in industrial waste stream as opposed to general removal of all cations, thus diminishing the capacity of the biosorbent for heavy metals removal.

When compared with a selection of biosorbents of plant origin, PSMC showed comparable maximum uptake capacity with those shown in Table 5. Both ion-exchange and chelation/complexation were suggested as the major mechanism of biosorption by these authors. Therefore, further characterization on the kinetic and surface characteristics of PSMC was done to shed light on the possible mechanism of nickel (II) uptake.

### Pseudo-second order kinetic model

Figure 7 shows regression of linearized pseudo-second order kinetics. Based on slope and intercept calculation, the \( q_e \) value, pseudo-second order constant rate and coefficient of determination value were 1.62 mg/g, 22.15 g/mg/min and 0.9999 respectively. The theoretical \( q_e \) value of 1.62 mg/g was in excellent agreement with the experimental value of 1.64. This model implies that chemisorption which involved valence force through sharing of electron is the limiting factor for the biosorption process. These results infer that biosorption is a complex process that may involve several mechanisms such as physical adsorption, chemisorption and ion exchange simultaneously. Nuholglu & Malkoc (2009) and Reddad et al. (2002) not only expressed that pseudo-second order kinetic aptly describes the biosorption process for waste pomace and sugar beet pulp biosorbent respectively, but also suggest that the chemisorption and ion binding mechanism are involved in the biosorption process respectively.

### Characterization of the biosorbent

The FTIR spectra with several intense characteristic bands related to functional groups that were present in polysaccharides and proteins are illustrated in Figure 8. General alkyl, aliphatic alcohol with carbonyl substitution and carbonyl compounds were found on the surface of the biosorbent. After nickel (II) biosorption, these general alkyl, hydroxyl or amino compounds, aliphatic alcohol

### Table 5 | Langmuir isotherm parameters for nickel (II) biosorption at 25°C pH 4.5 and their comparison with other biosorbents used that were non-pretreated prior to the biosorption experiments

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>( q_e ) (mg/g</th>
<th>[mmol/g]</th>
<th>( R^2 )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawdust of deciduous tree</td>
<td>4.6</td>
<td>0.953</td>
<td>0.953</td>
<td>Bozic et al. (2009)</td>
</tr>
<tr>
<td>Sawdust of walnut</td>
<td>3.29</td>
<td>0.9754</td>
<td>0.9754</td>
<td>Yasemin &amp; Zeki (2007)</td>
</tr>
<tr>
<td>Olive stone waste</td>
<td>2.13 [0.0363]</td>
<td>–</td>
<td>–</td>
<td>Fiol et al. (2006)</td>
</tr>
<tr>
<td>Sawdust of maple</td>
<td>0.27</td>
<td>0.9536</td>
<td>0.9536</td>
<td>Shukla et al. (2005)</td>
</tr>
<tr>
<td>Industrial raw kraft</td>
<td>3.76 [0.064]</td>
<td>0.978</td>
<td>0.978</td>
<td>Betancur et al. (2009)</td>
</tr>
<tr>
<td>PSMC</td>
<td>3.04</td>
<td>0.9992</td>
<td>0.9992</td>
<td>This study</td>
</tr>
</tbody>
</table>
and carbonyl compounds were identified as the active binding sites for nickel (II) biosorption. This result is supported by observation of nickel (II) biosorption occurring even at pH below 4 in Figure 3 which indicates other functional groups present as active binding sites besides carbonyl groups. Rehman et al. (2006) and Zakaria et al. (2009) reported similar functional groups of biosorbent in the study for Dalbergia sissoo and rubber tree sawdust respectively. The biosorption process mainly accounted for by ion exchange with calcium (II) ions as biosorbent has excessive calcium (II) ions. A significant release of calcium (II) ions from the biosorbent was observed after nickel (II) biosorption. This infers the displacement of calcium (II) ions by nickel (II) ions which strongly indicates an ion exchange mechanism, whilst the shifts observed for the hydroxyl or the amide bond might be due to chelation/complexation on the biosorbent surface. It is not unexpected of the biosorbent material to exhibit such characteristics as there are functional groups from lignin, cellulose and amino compounds that can play a major role in binding with nickel (II) ions intensively through an ion exchange mechanism. Similar phenomenon was reported by Fiol et al. (2006) which utilized olive stone biosorbent.

**Comparison of nickel (II) uptake by SMC with Amberlite IRC-86**

In light of the findings of the characterization studies, which indicates PSMC as having weak ion exchange capacity, its ion exchange performance was evaluated against a commercially available weakly acidic cation exchanger, Amberlite IRC-86. The biosorption percentages and the specific uptake obtained are shown in Table 6.

The uptake capacity obtained for both the Amberlite IRC-86 resin and PSMC are comparable, at 1.53 mg/g.

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Comparison of nickel (II) uptake and biosorption percentages of PSMC with Amberlite IRC-86</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSMC</td>
</tr>
<tr>
<td>Percentage biosorption (% ± SD)</td>
<td>45 ± 0.39</td>
</tr>
<tr>
<td>Uptake mg/g ± SD</td>
<td>1.53 ± 0.01</td>
</tr>
<tr>
<td>Estimated cost per gram</td>
<td>1X (~USD 27)</td>
</tr>
<tr>
<td>pH of solution before sorption</td>
<td>4.38 ± 0.01</td>
</tr>
<tr>
<td>pH of solution after sorption</td>
<td>4.57 ± 0.01</td>
</tr>
<tr>
<td>Reusability</td>
<td>Possible</td>
</tr>
</tbody>
</table>

Whilst a pH change of one unit was observed for the ion exchange resin, the PSMC did not produce similar changes in the pH of the solution. However, as discussed under the characterization of PSMC, increase in calcium (II) concentration was observed post biosorption for PSMC (data not presented). The reduction in pH is expected post sorption for the Amberlite IRC-86 ion exchange resin, as protons are readily exchanged for the heavy metal cations during the process. In the PSMC biosorbent, existing divalent and monovalent ions such as calcium (II) can be exchanged for nickel (II), since the PSMC used was not acid charged prior to biosorption use. This however, does not exclude the possibility of other mechanisms involved in nickel (II) biosorption for PSMC. Cost estimates for comparison with Amberlite IRC-86 ion-exchange resin, which has equal uptake capacity, in terms of cost per unit of metal removed, indicates that PSMC is at least six times less costly than the ion exchange resin. Whilst we did not evaluate for the reusability of PSMC, there is evidence in the literature which indicates the possibility of several biosorption–desorption cycles for biosorbents composed of fungal mycelia and sawdust (Shukla et al. 2002; Wang & Chen 2009). Even without desorption, PSMC can potentially still be competitive, especially for pre-treatment or combined treatment of heavy metal contaminated wastewater.

**CONCLUSION**

The approach of using the half-saturation concentration of biosorbent as the starting point for a rapid systematic evaluation of a biosorbent was successfully applied in the study of PSMC to determine the uptake, kinetics and mechanism of nickel (II) biosorption from aqueous solution. Fifty per cent of nickel (II) biosorption was attained at half-saturation constant of 0.7 g biosorbent concentration, initial pH of 4 to 8, 10 min contact time and initial concentration of 50 mg/L of 50 mL nickel (II) solution. Nickel (II) biosorption was fitted well to the Langmuir isotherm and pseudo-second order kinetics. The general alkyl, hydroxyl or amino compound, aliphatic alcohol and carbonyl compound in lignin, cellulose and protein play an important role in nickel (II) biosorption. Thus biosorption of nickel (II) involved several mechanisms simultaneously such as physical adsorption, chemisorption and ion exchange. A simple cost comparison for PSMC with Amberlite IRC-86 ion exchange resin that has comparable uptake indicates that the biosorbent has potential to be developed into a cost effective, environmentally friendly treatment system.
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